HE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY

. 181 June, 1943 Vol. XXVI

# *Minyulite (hydrous K-Al fluophosphate) from South Australia.*

By L. J. Spencer, F. A. Bannister, M. H. Hey,

and Miss Hilda Bennett.

Mineral Department of the British Museum.

[Read November 5, 1942.]

N 1908, at the close of the Franco-British Exhibition at Shepherd's Bush, London, a series of rock phosphates from various localities in South Australia s transferred to the Mineral Department of the British Museum as a present m the Government of South Australia. One large block from Wait's quarry Noarlunga,[1] 20 miles south of Adelaide, showed cavities lined with crusts of nute crystals. These crystals were determined goniometrically and optically 1908 to be orthorhombic, and qualitative chemical tests showed the presence of , Mg, P, F, and $H_2O$ (K was missed). This evidently represented a new mineral, d it is only now that the work has been successfully completed by the three nior authors. In the meantime, however, the same mineral was discovered in estern Australia by the late Dr. E. S. Simpson[2] in 1932, and named minyulite, m Minyulo Well. This he determined optically to be orthorhombic, and the rmula was given as $KAl_2(OH,F)(PO_4)_2.3\frac{1}{2}H_2O$ or $2K(OH,F).4AlPO_4.7H_2O$. ystallographic and X-ray data are now given for this species.

The large block (no. 18) was broken up and several hand-specimens (B.M. 09,53) were retained for the collection. Lining small cavities and filling veinlets the compact buff-coloured rock phosphate is a thin layer of opaque white atite with a finely fibrous structure normal to the layer, and sometimes showing mamillated surface. A few minute needles of wavellite (determined by X-rays) e also present. The minyulite crystals form a thin continuous crust on this atite, with the crystals closely and confusedly crowded together. It is present only a few of the cavities and in sparing amount. The crystals are colourless d transparent (water-clear) with a bright vitreous lustre. They are of a short-ismatic habit with a length less than 1 mm. and a width of about one-half or e-third of their length. Although the crystals are so brilliant only approximate

[1] The rock phosphate deposit associated with Cambrian rocks with overlying Tertiary beds this locality has been described in detail by R. L. Jack, The phosphate deposits of South ıstralia. Bull. Dept. Mines, South Australia, 1919, no. 7, 136 pp. (pp. 112–115).

[2] E. S. Simpson and C. R. LeMesurier, Minyulite, a new phosphate mineral from Dandagan, W.A. Journ. Roy. Soc. Western Australia, 1933, vol. 19 (for 1932–33), pp. 13–16. .A. 5–293.]

goniometric measurements could be obtained. Images are multiple due to si parallel growth, and are further confused by reflection from the back fac Only three crystal-forms are present: $m(110)$, $c(001)$, and $p(111)$. One series measurements on three crystals gave the mean values $cp$ 39° 22′, $mm$ 85° (corresponding to $a:b:c = 0{\cdot}926:1:0{\cdot}557$); and on another crystal $cp$ 39° 1 $mm$ 87° 24′ ($a:b:c = 0{\cdot}956:1:0{\cdot}563$). The second of these approximate ax ratios is nearer to those obtained by Mr. Bannister by X-ray methods (p. 31 There is a perfect cleavage parallel to (001). Etched figures produced by t action of hydrochloric acid on the prism faces (fig. 1) suggest that the cryst are hemimorphic; but on at least one of the measured crystals $p$ faces were fou at both ends.

The prismatic crystals show straight optical extinction with negative elon tion. The optic axial plane is parallel to (100) and the acu positive bisectrix is normal to (010) with large axial ang Refractive indices determined by the Duc de Chaulnes meth by focusing on etched figures through the prism faces (throu a thickness of 0·16 mm.) gave 1·5 and 1·6 as approxima values. Mr. Bannister has recently obtained by the immersi method the values $\alpha$ 1·525, $\gamma$ 1·530, and has confirmed that is large with positive sign. The specific gravity was determin as 2·46 by the pyknometer method on 1·658 g. of separat material.

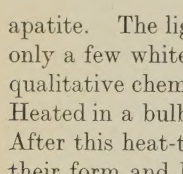



Fig. 1. Crystal of minyulite showing etched figures.

Material chiselled out of the crystal-lined cavities w separated in diluted methylene iodide from the associat apatite. The lightest fraction consisted of a nearly pure crystalline powder wi only a few white and yellowish grains. A portion of this material was used f qualitative chemical tests. The mineral is soluble in warm dilute HCl or HNO Heated in a bulb-tube it readily gives off water which is acid and etches the gla After this heat-treatment the crystals are white and opaque, but they still reta their form and bright lustre. Before the blowpipe it is difficultly fusible to blebby glass. One gram of the material was heated at different temperatur with the following results:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Temperature | ... | 110° | 150° | 182° | 219° | 235° | 243° | Redness |
| Loss in weight | ... | 0·4 | 0·6 | 13·7 | 16·6 | 17·5 | 18·2 | 19·8 % |

At redness over the Bunsen burner for ½ hour the material was partly fused the surface, and after a second ½ hour it was completely fused (sintered) on t surface.

This ignited material remained in the porcelain crucible until 1941, when it w used for the analysis made by Miss Bennett. Heated over a Meker burner the was a further slight loss bringing the total loss up to 20·4 %. As the presence potassium was not suspected her first analysis showed a low summation; h second analysis is given under I in table I. This as recalculated by Dr. Hey lea to the formula $K_2Al_4(PO_4)_4(OH,F)_2.8H_2O$, which also represents the contents the unit cell determined by X-rays. It differs from Dr. Simpson's formula on in showing one more molecule of water.

The habit of the crystals from Western Australia differs from that of t South Australian occurrence. The former occur as radiating groups of fine fibr

TABLE I. Chemical analysis of minyulite from South Australia.

| | I. | II*a*. | II*b*. | III. |
|---|---|---|---|---|
| $P_2O_5$ ... | 43·18 | 38·00 | 38·77 | 38·07 |
| $SO_3$ ... | 34·01 | 27·79 | 28·36 | 27·32 |
| $Al_2O_3$ ... | 0·91 | 0·80 | 0·82 | — |
| FeO ... | 0·09 | 0·08 | 0·08 | — |
| MgO ... | 0·86 | 0·76 | 0·77 | — |
| $Na_2O$ ... | 0·27 | 0·24 | 0·24 | — |
| CaO ... | 12·00 | 10·35 | 10·56 | 12·62 |
| ... | n.d. | 2·7 | 2·7 | 2·55 |
| $H_2O$ ... | — | 20·4 | 18·8 | 20·51 |
| $F_2$ ... | 5·44 | — | — | — |
| | 96·76 | 101·12 | 101·10 | 101·07 |
| less O for $F_2$ | — | 1·1 | 1·1 | 1·07 |
| | | 100·0 | 100·0 | 100·0 |

| | IV*a*. | | IV*b*. | |
|---|---|---|---|---|
| P ... | 4·01 | | 4·09 | |
| Al ... | 4·09 | 4·17 | 4·17 | 4·25 |
| Fe ... | 0·08 | | 0·08 | |
| Mg ... | 0·01 | | 0·01 | |
| Ca ... | 0·10 | 1·82 | 0·10 | 1·85 |
| Na ... | 0·06 | | 0·06 | |
| K ... | 1·65 | | 1·68 | |
| F ... | 1·1 | 2·0 | 1·1 | 2·0 |
| OH ... | 0·9 | | 0·9 | |
| O ... | 16·2 | | 16·6 | |
| $H_2O$ ... | 8·0 | | 7·4 | |

I. Analysis of the ignited material (0·2500 g.), by Miss Hilda Bennett; alkalis by M. H. Hey. The material had lost 20·4 % on ignition and still contained some fluorine. A fluorine determination made on 10 mg. of the original un-ignited material gave F 2·7 % approximately.

II. Analysis I recalculated (by M. H. Hey) deducting $SiO_2$ and some $Al_2O_3$ and $K_2O$ representing fragments of porcelain from the broken crucible in which the material had sintered: (*a*) on the assumption that no fluorine was lost on ignition; (*b*) that all the fluorine was lost. Since acid water is expelled on heating, whilst fluorine was shown to be still present in the ignited material, the true composition must be between II*a* and II*b*.

III. Calculated percentage composition for the formula $K_2Al_4(PO_4)_4(OH,F)_2{\cdot}8H_2O$ with OH:F = 1:1.

IV *a* and *b*. Number of atoms per unit cell calculated from II*a* and II*b*, sp. gr. 2·46, and the unit-cell dimensions *a* 9·35, *b* 9·74, *c* 5·52 Å.

sembling wavellite in appearance, on the surface of crevices in phosphatic nstone; but the essential characters are the same for both.

| | Western Australia (E. S. Simpson). | South Australia. | |
|---|---|---|---|
| $\alpha$ ... ... | 1·531 | 1·525 | (F. A. B.) |
| $\beta$ ... ... | 1·534 | — | (F. A. B.) |
| $\gamma$ ... ... | 1·538 | 1·530 | (F. A. B.) |
| Sp. gr. ... | 2·45 | 2·46 | (L. J. S.) |

Dr. Simpson stated that the fibres gave straight extinction with negative elongaon. His rather higher values for the refractive indices may be related to the wer amount of fluorine present. In the analysis by LeMesurier (table III) uorine is listed as a 'trace' and the summation is low; but it is stated that when e mineral was dissolved in $H_2SO_4$ glass was etched, and when it was heated uch acid water, also etching glass, was given off, suggesting the presence of ore than a 'trace' of fluorine, as further implied by the formula that was given. The mean refractive index of fluorine-free minyulite, calculated by Dr. Hey om the refractive indices determined by Mr. Bannister (mean $(\alpha+\gamma)/2 = 1{\cdot}527_5$) d the specific refractive energies ($k = (n-1)d$) $H_2O$ 0·340, O 0·203, F 0·043, ted by Larsen and Berman,[1] is 1·540. Simpson found $(\alpha+\beta+\gamma)/3 = 1{\cdot}534$, hich suggests that his fluorine content is much more than a 'trace'—in fact, it ay be round about 1 or $1\frac{1}{2}$ %.

[1] E. S. Larsen and H. Berman, The microscopic determination of nonopaque minerals. d edit., Bull. U.S. Geol. Surv., 1934, no. 848, p. 31.

X-ray examination of the crystals from South Australia has recently be undertaken by Mr. Bannister. Laue photographs confirm the orthorhomb symmetry and rotation photographs give the dimensions of the unit cell $a$ 9·35, $b$ 9·74, $c$ 5·52 Å.$\pm$0·02, cell volume 502·7 Å.$^3$, $a:b:c = 0{\cdot}960:1:0{\cdot}56$

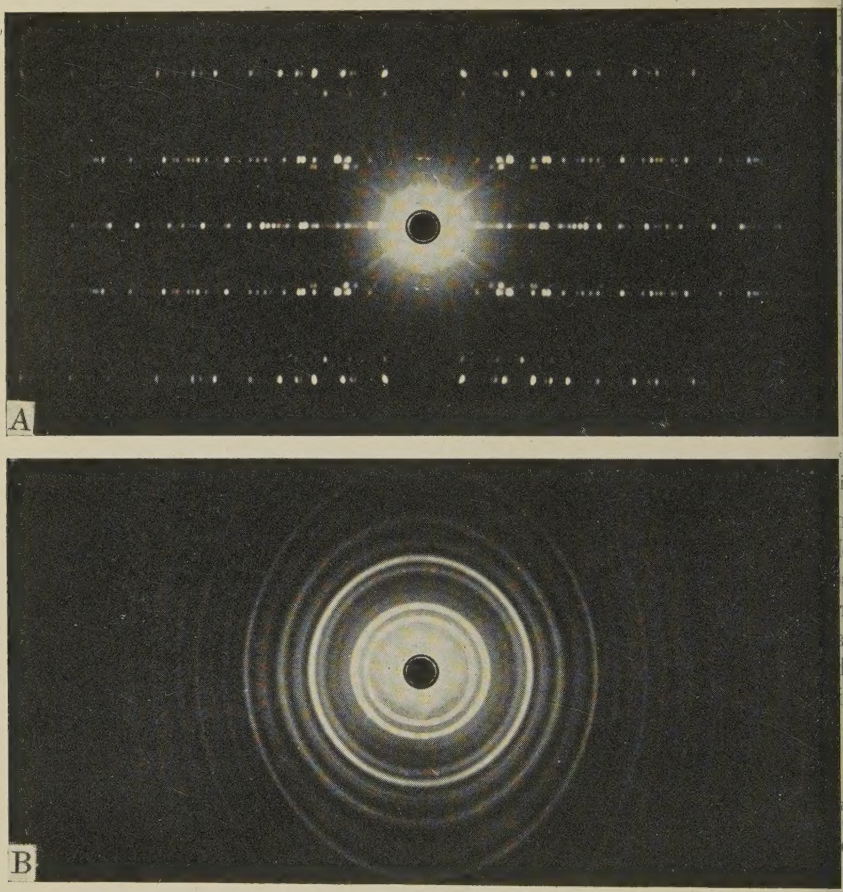



Fig. 2. X-ray photographs of minyulite from Wait's quarry, Noarlunga, South Australi (A) rotation photograph [001] of a single crystal; (B) powder photograph. Films taken wi unfiltered copper radiation, $\lambda$ 1·539 Å., in a cylindrical camera, 6 cm. diameter. Actual siz

Fig. 2A reproduces the rotation photograph of a crystal of minyulite about t $c$-axis. Oscillation photographs show that there are no halvings; hence t space-group is $C_{2v}^1 = Pmm$, which permits the following positions for the ur cell contents: 2K in a two-fold position $e, f, g$, or $h$; 4Al in a general position, $4(PO_4)$ in a general position, $i$; 2(OH,F) in a two-fold position $e, f, g$, or $h$; $8H_2$ in two sets of general positions, $i$.[1] None of the atoms is fixed by symmetry co

[1] Internationale Tabellen zur Bestimmung von Kristallstrukturen. Berlin, 1935, vol. p. 103. [M.A. 6–145.]

tions and sixteen parameters would need to be calculated from intensity data order to determine the crystal-structure.

Table II gives the spacings and intensities of powdered minyulite (fig. 2B) which e identical with those obtained for the original minyulite from Western ustralia, a paratype of which was presented by Dr. Simpson to the British useum in 1933 (B.M.1933,84). A rotation photograph of a small splinter of the tter specimen shows that the elongation of the needles making up the stellate ggregates is *c*[001]. It is doubtful whether this specimen would yield a single rystal fibre suitable for the X-ray determination of symmetry and of axial ratios.

BLE II. X-ray powder photograph of minyulite (fig. 2B). Spacings in Ångström units and timated intensities. Taken with unfiltered copper radiation, $\lambda$ 1·539 Å., in a cylindrical camera, 6 cm. diameter.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 6·8 | m | 2·59 | m | 1·57* | m | 1·209 | m | 0·984 | vw |
| 5·6 | vs | 2·43 | m | 1·498 | vw | 1·186 | m | 0·958 | m |
| 4·8* | w | 2·25 | | 1·478 | m | 1·165 | w | 0·943 | vw |
| 4·19* | w | 2·12 | m | 1·432 | m | 1·131* | vw | 0·932 | vw |
| 3·72* | m | 2·01 | w | 1·387* | vw | 1·110 | w | 0·919 | w |
| 3·37* | vs | 1·91 | w | 1·332* | m | 1·069 | w | 0·901* | w |
| 3·04 | w | 1·81 | w | 1·300 | w | 1·049 | vw | 0·884 | vw |
| 2·94 | w | 1·74 | w | 1·278 | vw | 1·036 | vw | 0·870 | w |
| 2·85 | vw | 1·69 | m | 1·259 | w | 1·021 | w | 0·861 | w |
| 2·69 | m | 1·61 | w | 1·237 | w | 0·999 | vw | 0·851 | w |

* Doublets. Bracketed lines are unresolved bands consisting of several lines, and the pacings and intensities of the limits are given.

In conclusion, table III collects together for direct comparison the several ublished chemical analyses of hydrous K-Al phosphates. If found in quantity iese minerals[1] (especially minervite, which contains also ammonium and occurs n recent guano deposits) would be of value as fertilizers for plant growth. -ray, optical, and density data have been determined by Mr. Bannister for such f these minerals as are available in the British Museum collection. All of them are istinct from minyulite. Details will be given in a later paper.

TABLE III. Chemical analyses of hydrous K-Al phosphates.

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. | XI. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $_2O_5$ ... | 38·00 | 35·58 | 35·05 | 37·28 | 35·17 | 42·70 | 40·85 | 37·10 | 37·89 | 34·64 | 33·60 |
| $l_2O_3$ ... | 27·79 | 29·98 | 21·43 | 18·59 | 18·18 | 21·00 | 20·59 | 22·89 | 25·21 | 27·79 | 36·03 |
| $e_2O_3$ ... | 0·80 | trace | 4·45 | 0·83 | — | 2·90 | 0·19 | 1·17 | — | — | — |
| gO ... | 0·08 | nil | — | 0·33 | trace | — | — | trace | trace | nil | 0·22 |
| aO ... | 0·76 | nil | 0·55 | 1·40 | 0·31 | — | — | trace | 12·80 | 18·10 | 6·80 |
| $a_2O$ ... | 0·24 | 0·45 | trace | — | — | — | — | 0·02 | 1·56 | 3·08 | 3·00 |
| $_2O$ ... | 10·35 | 12·30 | 4·20 | 8·28 | 5·80 | 1·20 | 8·95 | 8·04 | 4·84 | 2·25 | 1·64 |
| $NH_4)_2O$ | — | — | — | 0·52 | 0·48 | 3·47 | trace | 0·90 | — | — | — |
| ... | 2·7 | trace | — | trace | — | — | nil | — | — | — | — |
| $_2O$ ... | 20·4 | 20·63 | 33·06 | 28·20 | 28·30 | 29·80 | 27·79 | 29·16 | 16·80 | 14·19 | 17·88 |
| sol. ... | — | — | 0·80 | 4·35 | 11·60 | — | 1·09 | 0·36 | 1·10 | 0·58 | — |
| | 101·12 | 98·94 | 100·00 | 99·78 | 99·84 | 101·07 | 99·46 | 99·64 | 100·20 | 100·63 | 99·17 |

I. Minyulite, Wait's quarry, Noarlunga, Adelaide Co., South Australia. Miss Hilda Bennett, recalculated by M. H. Hey.

II. Minyulite, Minyulo Well, Dandaragan, Western Australia. E. S. Simpson and C. R. LeMesurier, 1933 (loc. cit.).

[1] They also contain traces of magnesium, which in small amount is an essential constituent chlorophyll $C_{55}H_{72}O_5N_4Mg$.

III. Taranakite, Sugarloaves, Moturoa, New Plymouth, Taranaki, New Zealand. J. He and W. Skey, Reports of the Jurors, New Zealand Exhibition, 1865, Dunedin, 1 p. 423. Also Cl 0·46, $SO_3$ trace; iron as FeO.

IV. Minervite, Minerva grotto, Fauzan, dép. Hérault, France. A. Carnot, Ann. des Mi 1895, ser. 9, vol. 8, p. 319. Also Cl, $SO_3$ traces.

V. Minervite, Tour-Combes grotto, Misserghin, Oran, Algeria. A. Carnot, Compt. Re Acad. Sci. Paris, 1895, vol. 121, p. 153.

VI. Minervite, basalt cave, St. Paul, Reunion, Indian Ocean. F. Pisani, analyst. Lacroix, Bull. Soc. Franç, Min., 1910, vol. 33, p. 34.

VII. Minervite, Jenolan Caves, New South Wales. J. C. H. Mingaye, Rep. Australas Assoc. Adv. Sci., 1898, vol. 7, p. 230; Rec. Geol. Surv. New South Wales, 1899, 6, p. 113. Mean of two closely agreeing analyses.

VIII. Palmerite, Monte Alburno, Salerno, Italy. E. Casoria, Atti R. Accad. Georgo Firenze, 1904, ser. 5, vol. 1, p. 293; Ann. R. Scoula Sup. Agric. Portici, 1904, vol

IX. Englishite, Fairfield, Utah. E. S. Larsen and E. V. Shannon, Amer. Min., 1930, vol. p. 328. [M.A. **4**–343.]

X. Lehiite, Fairfield, Utah. Larsen and Shannon, ibid., p. 331.

XI. Millisite, Fairfield, Utah. Larsen and Shannon, ibid., p. 330.

# *An X-ray study of diamonds artificially prepared by J. B. Hannay in 1880.*[1]

(With Plate X.)

F. A. Bannister, M.A., F.Inst.P.,
Deputy Keeper, Mineral Department, British Museum,
and K. Lonsdale, D.Sc.,
Royal Institution, London.

[Read January 28, 1943.]

DURING the course of a general investigation by one of us (K. L.) of diamonds from various sources, using X-ray analytical methods, the inquiry arose as whether so-called artificial diamonds had ever been examined in this way. It was found that there was, in the Mineral Department of the British Museum, a glass slide bearing 12 minute specimens, labelled as being diamond, artificially prepared and presented by Mr. J. B. Hannay in 1880, presumably the remainder of those investigated by Prof. N. Story-Maskelyne, and referred to in a letter to the Editor of *The Times* which appeared in that paper on February 20, 1880, as follows:[2]

'Artificial production of the diamond.

Sir,—A few weeks since I had to proclaim the failure of one attempt to produce the diamond in a chemical laboratory. To-day I ask a little space in one of your columns in order to announce the entire success of such an attempt by another Glasgow gentleman.

That gentleman is Mr. J. Ballantine Hannay, of Woodbourne, Helensburgh, and Sword-street, Glasgow, a Fellow of the Chemical Society of London, who has to-day sent me some small crystallized particles presenting exactly the appearance of fragments of a broken diamond.

In lustre, in a certain lamellar structure on the surfaces of cleavage, in refractive power, they accorded so closely with that mineral that it seemed hardly rash to proclaim them even at first sight to be diamond. And they satisfy the characteristic tests of that substance. Like the diamond, they are nearly inert in polarized light, and their hardness is such that they easily scored deep grooves in a polished surface of sapphire, which the diamond alone can do. I was able to measure the angle between the cleavage faces of one of them, notwithstanding that the image from one face was too incomplete for a very accurate result. But the mean of the angles so measured on the goniometer was 70 deg. 29 min., the correct angle on a crystal of the diamond being 70 deg. 31·7 min. Finally, one of the particles, ignited on a foil of platinum, glowed and gradually disappeared exactly as mineral diamond would do.

There is no doubt whatever that Mr. Hannay has succeeded in solving this problem and removing from the science of chemistry an opprobrium so long adhering to it; for, whereas the larger part of the great volume recording the triumphs of that science is occupied by the chemistry of carbon, this element has never been crystallized by man till Mr. Hannay achieved the triumph which I have the pleasure of recording to-day. His process for effecting this transmutation, hardly less momentous to the arts than to the possessors of a wealth of jewelry, is on the eve of being announced to the Royal Society.

I am, Sir, your obedient servant,
Mineral Department, British Museum, Feb. 19.' N. Story-Maskelyne.

A previous letter, which appeared in *The Times* less than two months before this, on December 31, 1879, shows how thoroughly Prof. Story-Maskelyne

[1] A preliminary note 'Laboratory synthesis of diamond' appeared in Nature, London, 1943, vol. 151, pp. 334–335.

[2] Reprinted in Chem. News, 1880, vol. 41, pp. 97–98; Nature, 1880, vol. 22, p. 404; Journ. Soc. Arts, 1880, vol. 28, p. 289.

investigated another sample of 'artificial diamond' sent to him from a differ source,[1] and how downright he was in his rejection of the spurious claim, wh was subsequently withdrawn.[2] The text of this earlier letter is as follows:[3]

'THE SUPPOSED ARTIFICIAL PRODUCTION OF THE DIAMOND.

Sir,—I should be obliged if you would accord me space in *The Times* in order that I n answer a great number of letters and applications which have pursued me during the p few days on a subject of some little public interest, that subject being the asserted format of diamonds by a gentleman at Glasgow.

Some ten days ago I had heard nothing whatever of the claim of Mr. MacTear, of the Rollox Works, Glasgow, to the artificial production of the diamond. My name, however, already in several newspapers as that of a person in whose hands the asserted diamonds been placed for a decision as to their true nature. Ultimately a small watch-glass, wit few microscopic crystalline particles, came into my hands for this purpose from Mr. Waring Smyth, and subsequently a supply came to me direct from Mr. MacTear. I shall proceed state the results I have obtained from the examination of these.

Out of the first supply I selected by far the largest particle, one about 1-50th of an inch length, and it may be that I wasted some time in experimenting on this particle, as it mig not have been an authentic example of the "manufactured diamond", since it differed in so respects from the specimens I have since received direct from Mr. MacTear.

Now, firstly, the diamond excels all substances in hardness. Secondly, its crystals belo to the cubic system, and should not, therefore, present the property of doubly refracting lig Frequently, however, from the influence of strain within the crystal, caused by enclosed g bubbles or other causes, diamonds are not entirely without action on a ray of polarized lig sent through them. Finally, the diamond is pure carbon, and, as such, burns entirely aw when heated to a sufficiently high temperature in the air, and more vividly so burns or glo away when heated in oxygen gas.

The specimens I had to experiment upon were too light to possess appreciable weight, t small even to see unless by very good eyesight or with a lens, yet were, nevertheless, sufficien large to answer the three questions suggested by the above properties.

A few grains of the dust, for such the substance must be termed, was placed between a pl of topaz—a cleavage face, with its fine natural polish—and a polished surface of sapphire, a the two surfaces were carefully "worked" over each other, with a view to the production lines of abrasion from the particles between them. There was no abrasion. Ultimately t particles became bruised into a powder, but without scratching even the topaz. They are n diamond.

Secondly, some particles, more crystalline in appearance than the rest, were mounted on glass microscope slide, and examined in the microscope with polarized light. They acted ea and all powerfully in the manner of a birefringent crystal. It seemed even in one or two them that when they lay on their broadest surface (it can scarcely be called a "crystal face' a principal section of the section of the crystal was just slightly inclined to a flattish side of in a manner that suggested its not being a crystal of either of the orthosymmetrical system Be that as it may, it is not a diamond.

Finally, I took two of these microscopic particles and exposed them to the intense heat of table blowpipe on a bit of platinum foil. They resisted this attempt to burn them. Then, f comparison, they were placed in contact with two little particles of diamond-dust exceedi them in size, and the experiment was repeated. The result was that the diamond particl glowed and disappeared, while the little particles from Glasgow were as obstinate and unacte on as before. I had previously treated the specimen I have alluded to as the first on which experimented, by making a similar attempt in a hard-glass tube in a stream of oxygen, an the result was the same. Hence I conclude that the substance supposed to be artificiall formed diamond is not diamond and is not carbon; and I feel as confident in the results th obtained from a few infinitesimal particles that can hardly be measured, and could only b

[1] Chem. News, 1879, vol. 40, p. 306.

[2] A. H. Allen, On the artificial production of precious stones. Chem. News, 1880, vol. 4 pp. 68–69.

[3] Reprinted in Chem. News, 1880, vol. 41, pp. 4–5; Nature, 1880, vol. 21, pp. 103–10 Journ. Soc. Arts, 1880, vol. 28, p. 105.

eighed by an assay balance of the most refined delicacy, as if the experiments had been erformed on crystals of appreciable size.

Not content with merely proving what these crystalline particles are not, I made an xperiment to determine something about what they are.

Heated on platinum foil several times with ammonium fluoride they became visibly more inute, and a slight reddish-white incrustation was seen on the foil. At the suggestion of r. Flight, assistant in this department, a master in the craft of the chemical analyst, these ttle particles were left for the night in hydrofluoric acid in a platinum capsule. This morning ney have disappeared, having become dissolved in the acid, and on evaporation there is seen slight white incrustation, on the capsule, of the residuary fluoride. I have, therefore, no esitation in declaring Mr. MacTear's "diamonds", not only not to be diamonds at all, but to onsist of some crystallized silicate, possibly one resembling an augite, though it would be very ash to assert anything beyond the fact that they consist of a compound of silica, possibly more than one such compound.

The problem of the permutation of carbon, from its ordinary opaque black condition into at in which it occurs in nature as the limpid crystal of diamond, is still unsolved. That it ill be solved no scientific mind can doubt, though the conditions necessary may prove to be ery difficult to fulfil. It is possible that carbon, like metallic arsenic, passes directly into the ondition of vapour from that of a solid, and that the condition for its sublimation in the form f crystals, or its cooling into crystal-diamond from the liquid state, is one involving a com- ination of high temperature and high pressure present in the depths of the earth's crust, but ery difficult to establish in a laboratory experiment.

I am, Sir, your obedient servant,
Nevil Story Maskelyne.

lineral Department, British Museum, Dec. 30.'

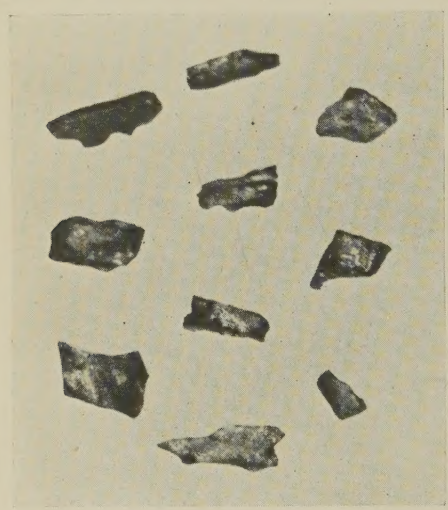
In view of the interest aroused in the subject at about that time, Story-Maske- yne's acceptance of the specimens submitted by Hannay as being genuine iamonds has all the more authority, since his investigation of them was cer- ainly as searching as possible.

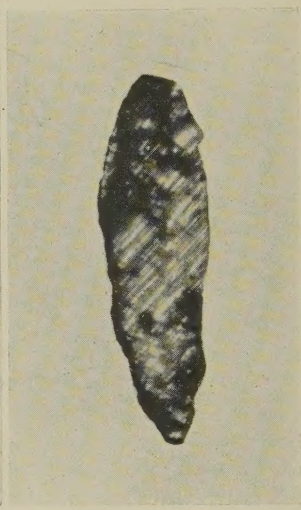
The twelve particles that remain from Story-Maskelyne's work in 1880 were ound mounted in Canada balsam on a glass slide. They are of irregular shape veraging in size $0{\cdot}4 \times 0{\cdot}2 \times 0{\cdot}1$ mm. (text-fig. 1). Unfortunately no account of heir identification by Story-Maskelyne is to be found in the records of the Mineral Department, and his correspondence with Hannay has not been traced. The glass slide is accompanied by a card label 'Hannay's artificial diamonds' in he handwriting of Thomas Davies, assistant in the department from 1862 to 892. The first examination of Hannay's specimens in London must have been arried out a few months before the removal of the Mineral collections from the British Museum, Bloomsbury, to the new building in South Kensington, in June 880. It is indeed fortunate that a few fragments mounted on glass should ave survived removal and that they were eventually catalogued, registered B.M.87756), and labelled by Dr. L. J. Spencer in 1901. Our recent re-examina- ion of the fragments not only places their identity beyond doubt but adduces ew evidence for the authenticity of their origin.

Examination of each particle in turn under the polarizing microscope prior to n X-ray rotation photograph, showed that all but one are isotropic, colourless, nd have the lustre and appearance of diamond. The X-ray photographs, as will be shown in detail later, confirm that eleven of the twelve are indeed diamond. The remaining buff-coloured birefringent particle has not yet been identified with certainty; possibly it is a fragment of some ceramic material. Several of the iamond particles have curiously striated cleavage faces (text-fig. 2) which in our pinion identifies the specimens satisfactorily with Hannay's material, for it is

precisely this feature which Story-Maskelyne commented upon in his descripti quoted above. That being so, it is of interest to consider Hannay's work from historical point of view and to find out, if possible, why he has never received t credit due to him for his success.

The experiments which led Hannay to take up this research are described two papers to the Royal Society.[1] His principal interest at this time was in t nature of the fluid state, as later papers show,[2] and he and a colleague, Jam Hogarth, had been engaged on the study of the solubility of solids in fluids abo their critical point. It occurred to him that carbon, hitherto so recalcitrant as





Hannay's artificial diamonds.

Fig. 1. Ten of the twelve fragments (B.M.87756) remaining from Story-Maskelyne tests. ×33.

Fig. 2. One of the fragments (the eleventh), which proved to be a mosaic type II diamon showing cleavage striations. Photographed in methylene iodide. ×100. (See pl. X, figs. and 5.)

solute, might dissolve in some fluid above its critical point, and might the crystallize out as diamond rather than as graphite when the temperature wa gradually reduced. Many experiments showed him that ordinary carbon (cha coal, lampblack, or graphite) was not affected by the most probable solvent chemical action taking the place of solution. He noticed, however, that when gas containing carbon and hydrogen was heated under pressure in the presenc of Li, K, Na, or Mg, the hydrogen combined with the metal and the carbon wa left free, being deposited in a particularly hard, scaly form. Then began a serie

[1] J. B. Hannay and J. Hogarth, On the solubility of solids in gases. Proc. Roy. Soc 1879, vol. 29, pp. 324–326; 1880, vol. 30, pp. 178–188.

[2] J. B. Hannay, On the state of fluids at their critical temperatures. Ibid., 1880, vol. 3 pp. 478–484. On the solubility of solids in gases, II. Ibid., 1880, vol. 30, pp. 484–489. On th limit of the liquid state. Ibid., 1881, vol. 31, pp. 520–522; 1882, vol. 33, pp. 294–321. On th absorption of gases by solids. Ibid., 1881, vol. 32, pp. 407–408. On the states of matter. Ibid 1881, vol. 32, pp. 408–413.

heart-breaking experiments 'On the artificial formation of the diamond', escribed in a preliminary note and in great detail in a later paper presented to he Royal Society,[1] which were communicated and read by Professor G. G. okes, then a Secretary of the Society.

Only three out of eighty experiments were at all successful; Hannay scrupu- usly describes those that were unsuccessful as well as those in which he believed had succeeded in obtaining diamond. In the experiment which gave him the rgest amount of solid diamantiferous material he used a mixture of 'paraffin irit boiling at 75°' (a mixture of light paraffins) 90 %, together with 10 % of refully rectified bone-oil[2] ('Bone oil . . . was distilled, and the portion boiling tween 115° and 150° was taken and rectified over solid caustic potash, and latterly ver sodium [until] free from moisture, oxygen, and sulphur'); these were placed, th 4 gm. metallic lithium, in a tube constructed on the gun-barrel principle wrought iron coil-tube) made of Lowmoor iron which he describes as 'very pure nd strong'. The dimensions of the tube were 20 inches long × 4 inches external iameter, ½ inch bore, and the mixture three-quarters filled it. After many efforts t obtaining an effective seal, he found that the best method of closing the tube as by welding, although this was a most difficult performance and, as he says, ay occasionally have introduced a little silica. The completely closed tube was hen placed in a tilted position in a large reverbatory furnace (which had to be built after some shattering explosions) the construction of which is minutely escribed, and heated to a 'dull red-heat' for fourteen hours, after which it was llowed to cool slowly. Many of his tubes exploded under this treatment; of hose that did not explode, 90 % were quite empty when they were opened, lthough a test by hydraulic pressure showed that there had been no leakage f any ordinary kind. What did happen, as he himself realized, of course, was hat at the dull red heat attained, the iron coil-tube became porous to gases (Proc. Roy. Soc., 1881, vol. 32, p. 407), and although Hannay tried various ways f lining his tubes (electroplating with Cu, Ag, Au; siliceous linings of fusible namels and glass) he only succeeded in retaining any liquid or condensed gaseous natter in the tubes in 4 out of 34 subsequent experiments.

However, in his few successful experiments the tubes, for some reason or other, *did* hold the pressure, for he writes:

'On opening the tube a great volume of gas was given off, and only a little liquid remained. *n the end of the tube which had been the upper end in the furnace* [our italics], the tube lying bliquely, there was a hard smooth mass adhering to the sides of the tube, and entirely covering he bottom. As I had never obtained all the solids in one piece before, I wished to examine it, nd so had the other end of the tube cut off, exposing the hard mass. It was quite black, and was removed with a chisel, and as it appeared to be composed principally of iron and lithium t was laid aside for analysis. I was pulverising it in a mortar, when I felt that some parts of he material were extremely hard—not resisting a blow, but hard otherwise. On looking closer, I saw that these were mostly transparent pieces imbedded in the hard matrix, and on triturating

[1] J. B. Hannay, On the artificial formation of the diamond. Proc. Roy. Soc., 1880, vol. 30, p. 188–189 (preliminary notice); 1880, vol. 30, pp. 450 461. Reprints or summaries of these papers appeared in Chem. News, 1880, vol. 41, pp. 106, 111; Nature, 1880, vol. 21, pp. 421–423, vol. 22, pp. 255–257.

[2] In Hannay's second paper these quantities are reversed, and have been so quoted subsequently by others, but it is clear from the context that only a relatively small percentage of bone-oil was actually used and that Hannay intended to give the figures as we have given them above.

them I obtained some free from the black matter. They turned out to be crystalline carb exactly like diamond.' (Proc. Roy. Soc., 1880, vol. 30, p. 458.)

'The carbon obtained in the successful experiments is as hard as natural diamond, scratch all other crystals, and it does not affect polarised light. I have obtained crystals with curv faces belonging to the octahedral form. . . . The crystals burn easily on thin platinum- over a good blowpipe, and leave no residue, and after two days' immersion in hydroflu acid they show no sign of dissolving, even when boiled. On heating a splinter in the elec arc, it turned black—a very characteristic reaction of diamond.' (Proc. Roy. Soc., 18 vol. 30, p. 189.)

A combustion conducted in pure oxygen, the crystals being laid on a th piece of platinum foil which was ignited by an electric current, showed that t sample used contained 97·85 % carbon, a very close approximation consideri the small quantity (14 mg.) available for test. The specific gravity, determin by flotation in a mixture of bromide and fluoride of arsenic, ranged as high 3·5. Hannay was not satisfied with the results of what he afterwards referred as 'that most troublesome investigation' (Proc. Roy. Soc., 1881, vol. 32, p. 40 and stated finally: 'I intend, when my other work—which I laid aside for t diamond experiments—is finished, to begin a series of experiments on the d composition of carbon compounds by metals, to find whether a more easily co trolled reaction may not be discovered' (Proc. Roy. Soc., 1880, vol. 30, p. 46 Apart from the 34 additional experiments mentioned above, in which he us tubes with various linings, it does not appear that Hannay ever carried out th intention.

It is noteworthy that Hannay regarded the presence of *nitrogen* as bei essential to the success of the experiment, though whether the nitrogen w believed by him to be an essential constituent of diamond (since he says that h final crystals contained a very small amount of nitrogen chemically combine or whether, as he says elsewhere, the carbon after being set free from th hydrocarbon has to be acted upon by a stable nitrogen compound in order tha it may be obtained in the clear, transparent form of the diamond, is not obviou from his description.[1]

In spite of Hannay's careful tests of his final material and of the confirmatio provided by Story-Maskelyne, his claim to have made diamond by a laborator method, seems never to have been taken seriously except, perhaps, by Moissa In 1902 we find Hannay complaining (Chem. News, 1902, vol. 86, p. 173) of statement made in the new volumes of the 'Encyclopaedia Britannica' (10t edition, article 'Gem, Artificial'), that the hard substance he found in his tube was really carborundum. 'Had the original paper or the correspondence i *The Times* been consulted,' he writes, 'this could hardly be asserted, as it wa fully tested at the time, and was found to be converted entirely into carbo dioxide when burnt in air or oxygen.'

In his Bakerian Lecture in 1918 Sir Charles Parsons[2] claims to have repeate Hannay's experiments but without success. He says (p. 77):

'Hannay's experiments were repeated, where paraffin and dipple-oil with the alkali metals especially potassium, were sealed in steel tubes and subjected to a red heat for several hours The analysis gave no diamonds; in fact it became apparent that when hydrocarbons or wate

[1] Compare W. H. Hudleston, Min. Mag., 1883, vol. 5, p. 209.

[2] C. A. Parsons, Experiments on the artificial production of diamond. Phil. Trans. Roy Soc., Ser. A, 1919, vol. 220, pp. 67–107. [M.A. 1–232.]

re relied on to produce pressure, the latter could only exist for a short time at the commencement, for when a red heat was reached the hydrogen escaped through the metal, and e oxygen combined with the steel. We did not analyse the steel tubes themselves. Many periments were, however, tried with central heating under the press at 6000 atmospheres, d nothing was obtained of interest with the substances used by Hannay, unless, as previously entioned, some iron was present.'

e have tried unsuccessfully to trace any of the products of Sir Charles Parsons's periments, but it is clear from his own statements[1] that Parsons was satisfied at in no case had he himself really succeeded in preparing diamond artificially, d he appears to have been equally convinced that no one else had done so her.[2] The article in 'Nature' referred to below states:

r Charles Parsons and Mr. [H. M.] Duncan have also repeated the experiments of other orkers who have claimed to have produced diamonds by artificial processes, but in every e the results have been negative. The conclusion seems inevitable that diamonds have not t been produced in the laboratory, and that investigators have been misled into regarding diamonds various transparent, singly-refracting minerals which happen to be very resistant chemical reagents.'

In the same article the writer suggests that spinels, which are formed at high mperatures from magnesia and alumina are exceedingly resistant to repeated eatment with concentrated hydrofluoric acid and boiling sulphuric acid, and at being colourless and cubic in structure they may easily be mistaken for iamonds; only the combustion test, which would leave such crystals unchanged, uld satisfactorily distinguish the genuine diamond.

X-ray analysis does, however, provide the means of making an even more ringent test. It is well known that every substance gives certain typical and nique diffraction patterns when irradiated by X-rays, the nature of the pattern epending upon the particular technique adopted. These patterns are most onveniently examined by means of photography. If, for instance, the substance s available in powder form only, the pattern recorded when a suitably prepared pecimen of the powder is irradiated by X-rays of a particular wave-length, onsists of a number of fine lines, the relative positions and intensities of which, y comparison with a card-index of patterns of known substances, can provide positive means of identification of the powder. The analogy with the 'finger-rint' method of criminal identification has actually led to the use of the term crystal finger-print' for a pattern of this kind. When the unknown substance is vailable in the form of small single crystals, other methods of identification are lso available. Firstly, the crystal may be mounted in a random orientation and hen rotated or oscillated during irradiation by X-rays of a particular wave-length. his will give, for diamond, a pattern of the kind shown in pl. X, fig. 5, which is btained using a circular camera with copper radiation. The spots correspond to eflections from particular planes of the crystal, their radial distance from the race of the undeviated beam gives a measure of the spacing of the planes, and heir intensity indicates the relative atomic densities of the planes. Thus by

[1] Quoted in an article on 'The problem of artificial production of diamonds'. Nature, 1928, ol. 121, pp. 799–800, signed C. H. D[esch]. [M.A. 4–68.]

[2] In the biography of Sir Charles Parsons by Rollo Appleyard ('Charles Parsons', Constable Co. Ltd., London, 1933) it is stated: 'At a meeting of the Royal Microscopical Society on pril 23, 1924, he [i.e. Parsons] said he had for twenty years been trying to make diamonds, nd had spent on his experiments £20,000, yet he had come to the conclusion that nobody ad ever made a diamond.'

means of X-rays not only the crystal form is ascertained, but also the distanc apart of the atoms, the arrangement of the atoms, and their actual atomic weigh No two known substances are composed of atoms of the same weights, arrang in the same way, and having the same interatomic distances, and any substan is therefore capable of unique identification by this means. Such a test sho that eleven of the twelve particles (B.M.87756) labelled as being the products Hannay's experiments are indeed diamond. In the case of four specime reflections foreign to the diamond pattern are present and these, though insuf cient in number for positive identification of the impurity giving them, might due to adherent or included magnetite and graphite, while one buff-coloure birefringent specimen, already mentioned, is not diamond at all and has not y been identified.

A second method of using single crystals for identification purposes is that the Laue photograph, for which white radiation (covering a range of wav lengths) is used with the crystal specimen stationary. Only one of the Hanna specimens (text-fig. 2 and pl. X, fig. 4) has been examined in this way, b the results are completely satisfactory. By mounting the crystal on a pair arcs it was found possible to orientate it (by calculation from random La photographs) so as to place a dyad axis vertical and thus to have four octahedr planes also vertical. The Laue photographs obtained with diamonds in th setting have recently been examined with the greatest thoroughness,[1] and th photographs of the particular Hannay specimen examined are typical of tho found for any natural diamond, allowance being made for the difference crystal size.

It is possible, however, by means of such Laue photographs, not merely t identify diamond as such, but also to distinguish ordinary diamonds from th rarer kind which has been classed by Robertson, Fox, and Martin[2] as type I 'transparent' diamond. Ordinary type I diamonds show, in addition to the usu Laue spots, various combinations of spots and streaks whose exact origin is n yet fully understood.[3] These extra spots and streaks are absent from Lau photographs of type II diamonds. The difference between the two types diamond is shown in pl. X, figs. 1 and 2. In order to take similar photographs the exceedingly minute Hannay diamond within a reasonable time, it was necessar to use an intensifying screen placed behind the 'duplitized' (i.e. sensitized o both sides) X-ray film, and photographs of a small natural diamond, similarl intensified, were taken for comparison purposes. It was quite clear from thes photographs, two of which are shown in pl. X, figs. 3 and 4, that the Hanna diamond examined is of the rare, 'transparent' type II. Further confirmation this fact was obtained by taking a Laue photograph of the Hannay diamon without intensification, in such a position that the (111) plane was exactly set fo selective reflection of Cu$K\alpha$ radiation. Previous comparison of a number o ordinary and rare type diamonds photographed in this position had shown tha although the (111) plane of an ordinary diamond reflects strongly, yet th

[1] K. Lonsdale, Proc. Roy. Soc., Ser. A, 1942, vol. 179, p. 315. [M.A. **8**–284.]

[2] R. Robertson, J. J. Fox, and A. E. Martin, Two types of diamond. Phil. Trans. Roy. Soc Ser. A, 1934, vol. 232, pp. 463 535. [M.A. **6**–6.] Further work on two types of diamon Proc. Roy. Soc., Ser. A, 1936, vol. 157, pp. 579–593. [M.A. **6**–494.]

[3] K. Lonsdale, loc. cit.; Proc. Physical Soc., 1942, vol. 54, p. 314.

eflection from a rare type diamond is very much stronger. The selective eflection from an ordinary type diamond is subject to what is known s 'extinction', whereas in the rare type diamond 'extinction' is small or bsent.[1] One consequence of this fact is that the 111 selective reflection om a rare type diamond, as recorded on a photographic film, is a spot surounded by a number of small concentric rings, the result of the diffraction of ne intense reflected beam by the black paper cover of the film-holder. These ngs are much more difficult to observe in the case of an ordinary type diamond, nd it is seldom that more than one is visible. The Hannay diamond, in spite of its xtreme smallness, gave a 111 selective (Cu$K\alpha$) reflection of such intensity that ot only had photographic reversal occurred, but the first *four* black paper rings ere easily observable. These indications that Hannay's artificially prepared iamond is of the more unusual 'transparent' type, are consistent with the observaon that these diamonds are optically isotropic, whereas ordinary type diamonds enerally show restoration of light, often to a considerable degree.[2]

The rarity of these 'transparent' diamonds (so-called because of their unusual ransparency in certain regions of the infra-red and ultra-violet spectrum) may e judged from the fact that Robertson, Fox, and Martin (loc. cit.), having obained one such diamond, examined between two and three hundred diamonds ithout finding another, although on further search they obtained five large and me small diamonds of the rare type, some from the Cape and others from Brazil. aman,[3] after examining several hundred diamonds at the Panna mines in entral India, obtained four plates of the 'transparent' type. Chesley,[4] in the ourse of an investigation of the minor elements in diamonds from various ources, found one 'transparent' diamond, and it is noteworthy that it was the urest of all the diamonds he examined. The absence of 'extinction' suggests hat the 'transparent' diamonds are of a more 'mosaic' structure than ordinary ype diamonds, and it is certain that crystals formed under laboratory conditions n which only small amounts of material are available and slow uniform rates of hange cannot be maintained for any considerable lengths of time, are much more kely to be 'mosaic' than 'perfect' in crystallographic structure. It is not urprising, therefore, that the Hannay diamond should prove to be of the mosaic', type II variety. Whether any of these artificial diamonds show nomalous spectroscopic effects cannot, unfortunately, be determined, as they ppear to be much too small for this kind of examination. No fluorescence could e observed when they were irradiated by X-rays (colourless diamonds of both ypes examined by one of us (K. L.) have always shown a blue-grey fluorescence nder irradiation), but this was possibly also due to their smallness, though it ight signify the absence of some impurity normally present in natural diamonds.

[1] The existence of extinction is the result of what the X-ray crystallographer calls crystal erfection'. By this is meant a uniformity of internal structure, without the slight changes f orientation or position that exist between the component crystallites of a 'mosaic' crystal. diamond may be 'perfect', in this sense, and yet show optical anisotropy, because of the xistence of a uniform internal strain; or it may be 'mosaic', and yet optically isotropic ecause the individual crystallites are unstrained.

[2] Compare G. Friedel, Bull. Soc. Franç. Min., 1924, vol. 47, p. 60 [M.A. 4–292]; Robertn, Fox, and Martin, loc. cit.; C. V. Raman, Current Sci., Bangalore, 1943, vol. 12, p. 41.

[3] C. V. Raman, Current Sci., Bangalore, 1942, vol. 11, p. 261.

[4] F. G. Chesley, Amer. Min., 1942, vol. 27, p. 20. [M.A. 8–268.]

Many of the Hannay diamonds show the (111) striations remarked on by Robertson, Fox, and Martin, as being typical of type II diamond. The interval between the striations is about 5$\mu$. The diamond shown in text-fig. 2 when examined by transmitted light reveals the cross-hatching of two sets of (111) cleavage striations.

We have definitely proved, therefore, that all but one of the specimens labelled as having been made artificially by J. B. Hannay in 1880 and presented by him to the British Museum are genuine diamond, one at least being a type II ('transparent' or 'mosaic') diamond. There seems to be no reason to doubt the genuineness of the specimens themselves; they correspond to Story-Maskelyne's description of them, as given in his letter to *The Times*; and various inquiries that we have made indicate that Hannay himself was a scientific man of integrity and that he genuinely believed that he had succeeded in his most difficult investigation. A suggestion made to us that these diamonds may have been fragments thrown into the tube by a workman who was tired of continual explosions, or 'seeds' put in to start crystallization, is negatived by the fact that Hannay obtained the diamonds from the solid mass at the *upper end* of the tilted tube and it is also rather improbable in that case that any of the 'seeds' would have chanced to be of the rare type II. We believe that J. B. Hannay did indeed make diamonds by a laboratory method and that the method he used is capable of giving the 'transparent' type which is apparently rare among natural diamonds, perhaps because the latter are so seldom really pure.

On the other hand, the difficulties which Hannay encountered, the low percentage of success in his numerous experiments, the failure of Sir Charles Parsons to repeat Hannay's method, and the minute amount of diamond which even the most successful experiments yielded, show that any hope of making artificial diamond on a large scale is hardly likely to be realized without considerable patience, perseverance, and expense.

## Explanation of Plate X.

*X-ray study of Hannay's artificial diamonds.*

The first four figures have been reproduced from Laue photographs comparing Hannay diamond with types I and II of natural diamond. The details of film and crystal setting for figs. 1–4 are: crystal to film distance 3 cm.; film-normal inclined 68° with the forward direction of the X-ray beam, the beam inclined 23·5° with the (111) plane and 11·75° with the (110) plane, the axis [110] of the diamond being vertical.

Fig. 1. Natural diamond type I. Photograph not intensified, 30 minutes exposure. Specimen D(2) of K. Lonsdale (loc. cit.). Weight 1 mg.

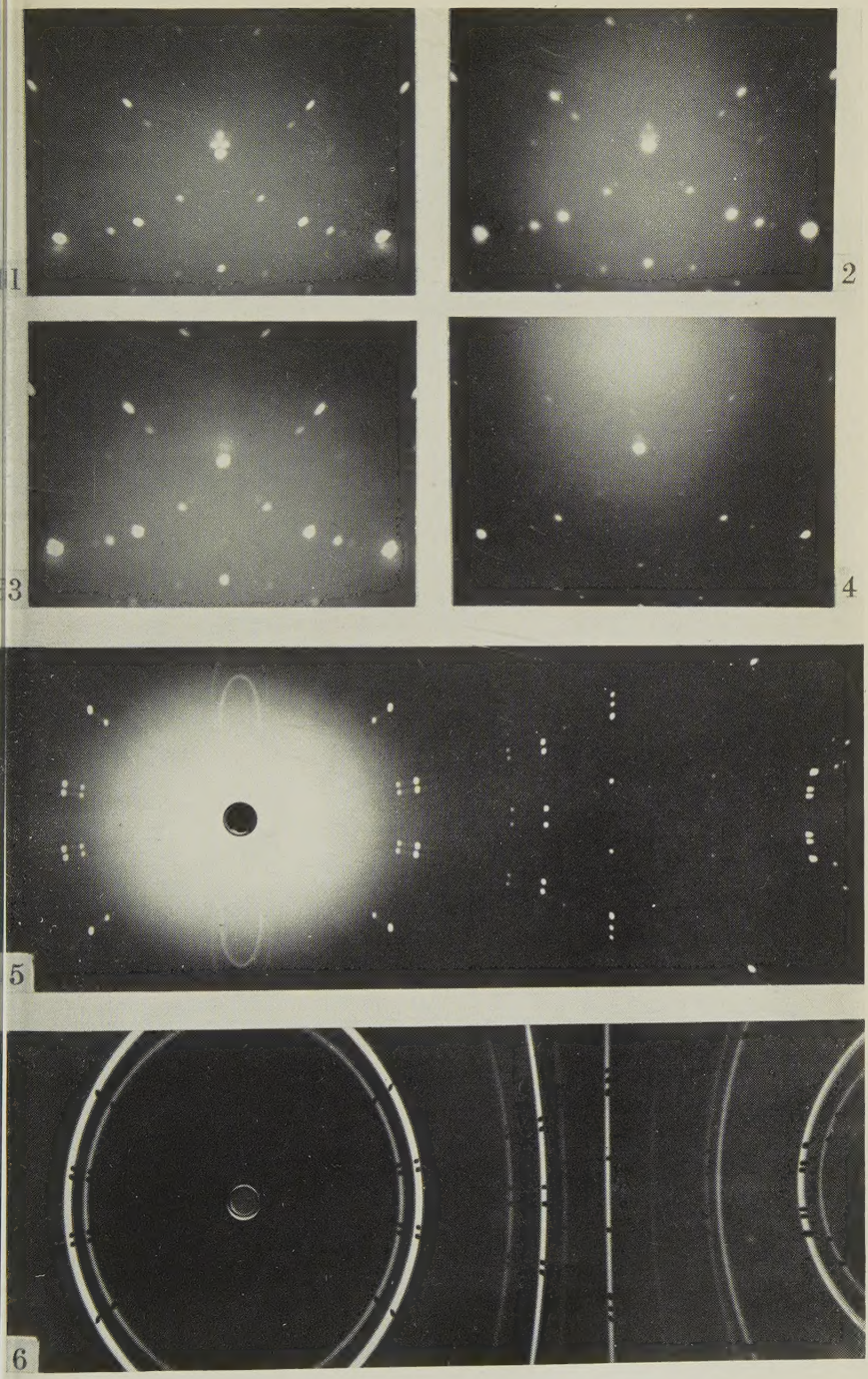
Fig. 2. Natural diamond type II. Photograph not intensified, 5 minutes exposure. Specimen D16 of Robertson, Fox, and Martin. Weight 0·6149 gm.

Fig. 3. Natural diamond type I. Photograph intensified by fluorescent screen, 5 minutes exposure. Specimen D(2). Weight 1 mg.

Fig. 4. Hannay's diamond (text-fig. 2). Photograph intensified, 30 minutes exposure. Weight less than 0·05 mg.

Fig. 5. Rotation photograph of Hannay's diamond (text-fig. 2) mounted in random orientation. Unfiltered copper radiation, camera diameter 6 cm. Actual size.

Fig. 6. Spots of fig. 5 reversed and superposed upon a powder photograph of natural diamond (commercial powder kindly supplied by Mr. B. W. Anderson). Cu$K\alpha$ and Cu$K\beta$ lines are present for the diffractions 111, 220, 311, 400, and 331.




F. A. Bannister and K. Lonsdale: X-ray photographs of Hannay's artificial diamonds.